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Calibrating the Pesticide Capture Efficiency of Passive Dosimeters

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Abstract: A system has been devised for determining the absolute capture efficiency of passive dosimeters. The system is composed of three components: a wind tunnel, a tracer atomizer, and a capture efficiency test device (CETD). The CETD consists of a series of cylinders separated by nylon screens to intercept and capture the spray containing a tracer. The decline in tracer at the screens was used to determine the tracer incident on the first screen. This in turn was used to estimate the tracer incident on a test dosimeter of washed muslin. The capture efficiency of the dosimeter was expressed as the ratio of tracer captured to tracer incident on the dosimeter. The capture efficiency of the test dosimeter using the CETD was found to be independent of the time of exposure and quantity of tracer captured.

The approach presented is novel in that the method for documenting capture efficiency does not require prior knowledge of the spray concentration. Elimination of this requirement allows the use of the device in a much larger array of test situations (e.g. field and greenhouse studies) than has been previously possible. Furthermore, the conceptual model can easily be modified to allow for capture efficiency measurements from a range of structures and materials such as plants or whole leaves, as well as insects and non-target animal species. The CETD is simple and portable and could be used to calibrate dosimeters in a variety of field situations.

Key words: calibration, capture, efficiency, passive dosimeter.

1 INTRODUCTION

Exposure assessment is a vital component of the quantitative risk assessment procedure contributing to pesticide regulatory decisions. A wide array of scientific disciplines is required to address the myriad complex and interacting parameters of oral, dermal, inhalation, acute and chronic exposures.[1] There are two major approaches to estimating exposure: passive dosimetry and biological monitoring (Table 1). Both approaches have advantages and disadvantages: passive dosimeters have the potential to produce definitive data on routes of exposure, while biological monitoring provides direct evidence of exposure. However, the linkage between capture data by passive dosimeters and definitive biological results, such as urinary metabolites, is often obscure and poorly correlated. Consequently, the reliability of patch techniques used to measure dermal exposure has been questioned.[2] A definitive study of capture efficiencies of passive dosimeters could bring clarity and understanding to some obvious differences now being encountered in passive versus biological monitoring studies. A step toward that goal is a usable and general method for estimating capture efficiency of all actual and potential dosimeters.

There are currently no data relating capture efficiency of any of the many patches in use to that of human skin and hair. The work of Fenske[3] on the correlation of tracer fluorescence on the skin and patch dosimeters illustrates the difficulties and importance of this information. This technique assumes that the relationship between the quantities of aerosol on skin and a patch is the same for the fluorescent tracer in water and for a formulated pesticide, which has not been verified. Furthermore, the wide disparity in capture efficiency of different dosimeters sampling different aerosols (including

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TABLE 1
Advantages and Disadvantages of Estimating Pesticide Exposure with Passive Dosimetry and Biological Monitoring

	Advantages	*Disadvantages*
Passive dosimetry	Routes and areas of exposure clearly defined*	Dermal and respiratory absorption must be estimated*
	Routine experimental design and execution	Extrapolation from patch to body surface area must be made
	Generic data bases may be created	Not all exposure scenarios are amenable
Biological monitoring	Actual dose may be measured*	Pharmacokinetics must be known*
	Unnecessary to adjust for value of garment/protective clothing	Routes of exposure cannot be distinguished
		Difficult to ensure participant cooperation
		Potential problems when using invasive techniques required for specimen collection

* Considered most important.

different combinations of pesticide and adjuvant) sprayed from different atomization devices greatly confounds the problem. The lower index of exposure of passive dosimeters versus that obtained by biological monitoring can be utilized to obtain valid exposure assessments only if adequate correlations with predicted risk of uptake are available. Biological monitoring, on the other hand, tends to be more chemical-specific. The overestimates of exposure seen in some studies,[3,4] leading to questions of reliability, may be due to the ability of certain materials to express differential capture efficiencies, contributing to a concentration effect. If the quantity deposited was correlated with that delivered on the basis of a capture efficiency index, then a more accurate predictability of exposure would be achieved.

In general, capture of particles by the surface of an object is related to the object shape, size, orientation to the wind, air flow through and/or around, and surface features as well as to particle characteristics and meteorological conditions.[5–10] These parameters are of interest when considering the behavior of dosimeters, because, even though the majority of materials used as passive dosimeters are man-made or highly processed, their surfaces may differ widely in their architecture and hence their ability to capture drops and/or particles.

Since the major route of application exposure is through operation of boom or especially air-blast sprayers, a standard method for quantifying the potential exposure from mists in the air as the operator traverses the field would be useful in aiding assessment of risk for such operations. Patches, rather than entire clothing, are likely to be the standard assessment protocol because of the problem of contamination involved in the removal of the suits, etc. Clearly, less troublesome and more accurate methods would improve the exposure estimating process. Data on capture efficiency of an array of patch simulations would allow a more accurate assessment of potential hazards from particular delivery systems and conditions. A study of the capture efficiency of the various patches, clothing, human skin and other exposure assessment devices (e.g. string) should give us a better understanding of why passive dosimeters tend to overestimate real exposure hazards (e.g. pads overestimating exposure to the head.[3,4]

A new method of exposure assessment is needed to take us beyond the very dated methodology of Durham & Wolfe.[11] Some passive dosimeters capture more spray droplets than others in the same spray cloud, and thus have higher efficiency, but unless the amount of spray *not captured* can be determined, neither their absolute nor their relative efficiencies can be determined. Capture efficiency (or impaction efficiency, E') has been defined[5] as the ratio of the mass (or number) of drops collecting on a surface, M_d, to the mass (or number) of drops incident on the area projected by the surface M_i, expressed as a percentage:

$$E' = 100 \cdot \frac{M_d}{M_i} \% \qquad (1)$$

The absolute measure of efficiency defined by eqn (1) has hitherto been rather unhelpful because of the difficulty in estimating M_i. Improvements in test methodology of exposure hazard assessment would prove invaluable in more accurately relating an operator's risks involved in pesticide use and application.

It seems likely that patches will continue to be a mainstay of pesticide exposure assessments for the foreseeable future. With that in mind, we report here a new method for estimating capture efficiency that will contribute to a better understanding of the differences between passive dosimetry and biological monitoring procedures. The objectives of this study were to develop a technique to measure the absolute capture efficiency

of passive dosimeters, as defined in eqn (1), that is easy to use and mathematically robust.

2 CAPTURE EFFICIENCY TEST DEVICE

2.1 Concept

Traditional devices and methods used for determining capture efficiency all require a precise knowledge of the amount of test substance introduced to the device as well as the amount collected by the test surface.[8] While the second requirement may be relatively easy to measure, the amount introduced is much more difficult to assess, and is usually estimated from the atomizer throughput or by summation of the amounts collected on the test surface and by the device as the spray clouds exits.[8] Both of these approaches introduce errors to the methodology that we feel are unsatisfactory. We sought to develop a device that would eliminate this requirement, thus increasing the accuracy and practicality of capture efficiency estimation.

The approach taken here integrates a test device, described in detail below, with a statistical procedure which provides a precise estimate of the amount of spray entering the device. The device comprises several serially located mesh screens in a cylinder through which a spray cloud passes. A test surface (dosimeter), placed in front of the first screen, captures a portion of the spray cloud as it enters the cylinder. As the spray cloud continues through the cylinder, each screen removes a portion of the drops (or particles) from the successively reduced population of drops present in the cloud. The amount of material extracted from each of the screens, reflecting the reduction in spray cloud density over time as it passes through the cylinder, is then used to estimate the amount of spray material incident on the first screen using a statistical analysis based on removal sampling.[12] This approach eliminates the need for precise measurement of the atomizer throughput and the resulting problematic estimates of the proportion incident on the dosimeter. Instead, we determine (precisely) how much spray *did not impact* on the dosimeter. It is then a rather simple matter to estimate the capture efficiency (eqn (1)) of the test sample from the amount of spray incident to the dosimeter and the amount recovered from it.

2.2 Description

The Capture Efficiency Test Device (CETD), shown in Fig. 1 consists of four serial cylinders, 11·3 cm in diameter and 10·0 cm long, which when assembled together form a single cylinder. Each cylinder is constructed in two sections such that a 'backup' screen can be clamped between the sections. The backup screens are nylon mesh (Petticoat Net, Montage, Inc. #219-0650) and serve as the spray cloud samplers from which the amount of spray entering the CETD is estimated. The choice of screen material was made based on mesh size (1·2 mm × 1·5 mm), which allowed air passage with only a 10% reduction in velocity, and on the high extraction efficiency, discussed below. When fully assembled, the device contains four, uniformly spaced (10 cm apart) backup screens and a sample of the material being tested centered in the air stream approximately 1·25 cm in front of the first screen (Fig. 1). The dosimeter, attached to a solid 2·2 × 2·2 cm mount, is situated at the opening of the first cylinder section of the CETD. To reduce turbulence within the CETD the leading cylinder has its outer leading edge bevelled so that the air flows smoothly around the entrance. During operation the CETD is placed in a wind tunnel downwind of a source of monodispersed (uniformly distributed in size and velocity, see Fig. 2) particles generated by a pesticide spray nozzle or atomizer.

2.3 Operation

In the field, the relative velocity governing impacts of spray droplets on a dosimeter is provided by the wind and motion of the operative. In the laboratory, the CETD is operated in a wind tunnel to provide the relative motion required to effect impact of the spray cloud on the dosimeter. The wind tunnel, constructed mainly of plywood with several Plexiglass observation windows, consists of a test chamber 0·61 m wide by 0·91 m high by 3·7 m long for conducting experiments. A 7·5 kW motor with variable-speed controller 4·5 m downstream of the test chamber draws air through it at velocities of up to 7 m s^{-1}. To minimize inherent turbulence, the tunnel has a 2·4 m long inlet contraction section containing 850 2·5 cm diameter tubes each 0·8 m long. The tunnel also has a biplane grid 0·7 m downstream from the tubes to produce the desired turbulence intensity and a uniform mean velocity profile.

During operation, the CETD and the atomizer are situated in the wind tunnel's observation chamber about 2 m apart. The atomizer is located 0·3 m above the floor and the test material, inside the CETD, is 0·25 m above the floor. A baffle system placed around the atomizer provides adjustment and control of the amount of spray material that is allowed to pass into the entrance of the CETD. The baffle opening is 1 cm × 3 cm.

Once the wind tunnel is started and has achieved the desired velocity, the atomizer is started at the desired voltage, allowed to come to speed, and the flow valve is opened. Run time of the atomizer may be varied as needed according to the tracer rate, amount of tracer desired on the target, and the atomizer baffle opening size. Once the run time has elapsed, the flow valve is closed and the atomizer turned off. Finally, the wind

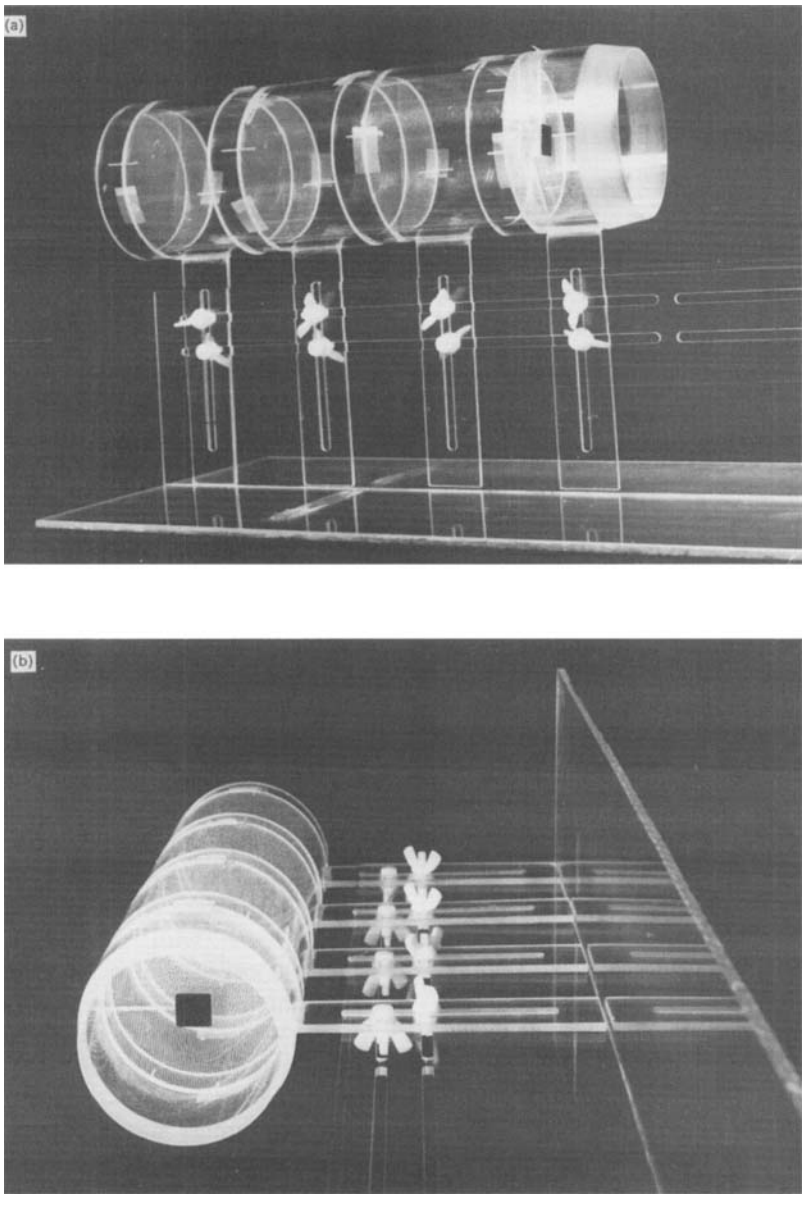

Fig. 1. Two views of the CETD: (a) side profile, (b) perspective. The cylinder sections slide together to form a single cylinder. The four backup screens can be seen, one in each cylinder. The test dosimeter is the black square suspended ahead of the screen in the first cylinder.

tunnel is turned off and the CETD removed. The test dosimeter and backup screens are then removed for fluorimetric analysis using a previously described method.[13] The quantities of tracer extracted from the test sample and backup screens are then used to calculate the sample capture efficiency.

3 THEORY AND STATISTICAL METHODS

3.1 Determination of capture efficiency

Capture efficiency is defined as the mass of material captured by an object (dosimeter) placed in the air stream relative to the mass of material incident to the dosimeter (eqn (1)). We express this here as E, the difference of the logarithms:

$$E = \log[M_d] - \log[M_i] = \log[E'] - 2 \qquad (2)$$

where M_d is the mass collected by the dosimeter and M_i is the incident mass. The mass incident to the dosimeter surface can be estimated from the total mass incident on the first backup screen, M_b. Total mass entering the CETD is thus

$$M_t = M_d + M_b \qquad (3)$$

The ratio of mass incident to the dosimeter, M_i, to mass entering the CETD, M_t, is given by the ratio of their areas of cross-section, A_i/A_t, from which M_i can be

calculated:

$$M_i = M_t \cdot \frac{A_i}{A_t} = M_t \cdot \frac{L^2}{\pi(D/2)^2} = M_t \cdot \frac{4L^2}{\pi D^2} \quad (4)$$

where D is the opening diameter of the CETD and L is the width of the dosimeter (assuming a square dosimeter surface). Combining eqns (2) and (4), the capture efficiency, E, is

$$E = \log[M_d] - \log[M_d + M_b] - \log[4L^2/\pi D^2] \quad (5)$$

for which the last term is a constant depending on the geometry of the CETD. Thus, E depends on the quantity of aerosol captured on the dosimeter, M_d, and the quantity, M_b, incident on the first backup screen.

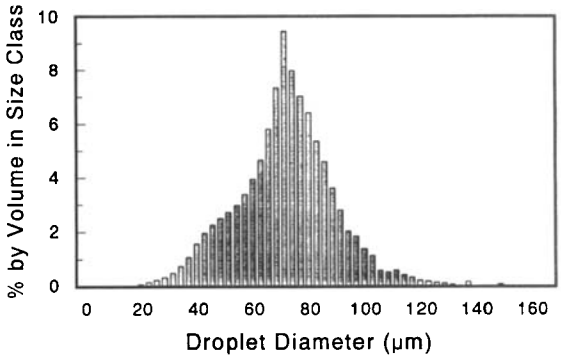

Fig. 2. Monodispersed droplet spectrum obtained using an Aerometrics PDPA 100-1D. Tracer with 0·25% Ortho X-77 were atomized using an 'Ulva'® spinning disc sprayer at 12 volts.

3.2 Statistical analysis

The mass incident on the first screen, M_b, can be estimated from the amount of tracer captured by the backup screens using a multinomial removal sampling model by either least squares (LS) or maximum likelihood (ML).[14]

3.2.1 Assumptions

The basic assumptions are:

1. The population of droplets sampled by backup screens is closed, i.e. there is no change to the population except the loss to screens;
2. The probability of capture by the ith screen is the same for all droplets;
3. The probability of capture is the same for all screens.

The practical consequence of assumptions 2 & 3 is that sampling is assumed to be a Poisson process in which the sampling effort is δf. The probability then of any individual droplet being caught is approximately $c\delta f$, where c is the catchability coefficient or sampling efficiency of the backup screens. The probability of an individual being caught in the ith sample is thus the zero term in the Poisson series:

$$p_i = 1 - q_i = 1 - e^{(-cf_i)} \quad (6)$$

A gain to the population of droplets could only occur by fission of droplets passing through a sampler; loss by deposition between samplers could occur as a result of a velocity drop as the stream passes through each sampler. However, no droplet loss was detected using water-sensitive paper applied to the inner surfaces of the device between the backup screens. Constant probability of capture for all droplets assumes constant size. The droplets were supposed to be monodispersed, but what this means in practice is that the distribution of droplet size is highly leptokurtic, with small standard deviation and little or no skewness (see Fig. 2). Droplets in the tails may either be too small to catch or so large and energetic that they pass right through the sampler, breaking up as they do so. Provided the sampling efficiency is not greatly dependent on velocity, the probability of capture will be the same for all four samples.

3.2.2 Statistical model

The joint probability of obtaining $\{m_s\}$, where m_s is the catch is sample s ($s = 1 \ldots k$, k = four screens), is the product:

$$f(\{m_s\}) = \prod_{s=1}^{k} f(m_s \mid M_s) \quad (7)$$

where

$$M_s = M - x_s \quad (8)$$

is the population of droplets available for capture at screen s, and

$$x_s = \sum_{i=2}^{s} m_{i-1} \quad (x_i = 0) \quad (9)$$

For $s = k$ samples, $f(m)$ is the multinomial distribution:

$$f(\{m_s\}) = \prod_{s=1}^{k} \binom{M_s}{m_s} p^{m_s} q^{(M_s - m_s)}$$

$$= \prod_{s=1}^{k} \frac{\left(M - \sum_{i=2}^{s} M_{i-1}\right)!}{m_s!\left(M - \sum_{i=1}^{s} m_i\right)!} p^{m_s} q^{(M - \Sigma_1^s m_i)} \quad (10)$$

Estimates of M and q ($\hat{M}$ and $\hat{q}$, respectively) are obtained by iterative solution of the ML equations:

$$\hat{M} = \frac{\sum_{s=1}^{k} m_s}{1 - \hat{q}} \quad (11)$$

$$\frac{\hat{q}}{(1-\hat{q})} - \frac{k\hat{q}^k}{1-\hat{q}^k} = \frac{\sum_{s=1}^{k}(s-1)m_s}{\sum_{s=1}^{k} m_s} \tag{12}$$

The variances are given by:

$$V[\hat{M}] = \frac{Mq^k(1-q^k)}{(1-q^k)^2 - (kp)^2 q^{(k-1)}} \tag{13}$$

$$V[\hat{q}] = \frac{(pq)(1-q^k)}{M\{q(1-q^k)^2 - (kp)^2 q^k\}} \tag{14}$$

Trial values of $\hat{M}$ and $\hat{q}$ may be obtained from the regression of x_s on m_s. This is shown in Fig. 3 (solid squares) in which the least squares regression line extrapolated to the abscissa gives the trial value, $M_0 = \bar{x} + \bar{m}/b$. The negative of the gradient b is the least squares estimate of the catchability coefficient, c.

An alternative approach is available which does not require iteration and gives a reliable estimate in most cases. It employs the fact that for $k = 4$, the left hand side of eqn (13) is approximately equal to $1{\cdot}5q$ for $0{\cdot}1 < q < 0{\cdot}9$. Thus $\hat{q}$ may be estimated from

$$\hat{q} \approx \frac{2\sum_{s=1}^{4}(s-1)m_s}{3\sum_{s=1}^{4} m_s} \tag{15}$$

and an approximate value for $\hat{M}$ obtained by substituting into eqn (12).

4 EXPERIMENTAL METHODS

To estimate the amount of spray entering the CETD, the amount of spray on the sample dosimeter and the backup screens must be determined. This was done by extracting the spray from the sample and screens and analyzing the wash by colorimetric analysis of the fluorescent tracer.[15] The amount of spray removed was then read off calibration curves.

4.1 Recovery curves for the tracer

The calibration curves were derived using a drop-on-demand device[16] to produce drops of ≈ 200 μm diameter on the screen and test materials. This droplet size was chosen to simulate exposure of the applicator, as opposed to mixer-loader exposure where most of the dose is acquired through larger drops and/or splashes. Thus the total amount of tracer on the target is likely to have been acquired as a result of exposure to a number of smaller droplets. The treatment solutions contained either ≈ 500 μg ml^{-1} or ≈ 2000 μg ml^{-1} 'Tinopal' CBS-X (Ciba-Giegy, Greensboro, NC). The latter concentration was used for drop numbers in the range of 334 to 17 drops per sample and the 500 μg ml^{-1} solution was used for 67 to 1 drop per sample. Each of these ranges was divided logarithmically to yield a total of 30 drop numbers (ie. 334, 239, 183 ... 3, 2, 1). Two different rates of tracer were used to ensure that the entire sensitivity range of the fluorimeter was utilized.

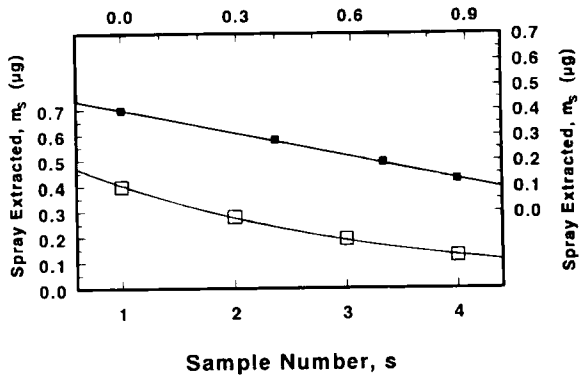

Fig. 3. The quantity of spray intercepted by the nylon backup screens in the cylinders (see Fig. 1) declines exponentially with sample number (open squares, left and lower axes). The quantity of spray removed by the screens is linearly related to the transformed (from eqn (8)) samples (solid squares, right and upper axes). The intercept of the straight (transformed) line with the abscissa is the quantity of spray incident on the first screen, which is calculated using eqn (11).

Droplets were applied to $2{\cdot}2 \times 2{\cdot}2$ cm samples of backup screen material. Three replicates were performed for each droplet number, giving a total of 90 samples. After droplet application, the samples were placed in 100-ml glass snap-cap jars and allowed to dry for c. 15 min before further processing. The tracer was extracted from each sample by agitating it for 2 min in a glass jar containing 10 ml distilled water. The jars were agitated using a mechanical shaker to ensure uniform extraction. The sample was then removed from the jar and 5 ml of the solution was dispensed into a cuvette (VWR borosilicate, Cat. No. 60825-550) for subsequent fluorimetric analysis. Samples were analyzed using a Turner 112 filter fluorimeter and a computerized data acquisition system. Three readings were taken on each sample, the mean of which was recorded as the fluorescence value.

To determine the actual drop size applied to the samples, c.100 drops were collected on water-sensitive paper (Spraying Systems Co., Wheaton, IL 60188) at random during the drop application process. The drop stains were measured using a 'Wild'® compound microscope equipped with a graticule. A spread factor of 2 was applied to the mean stain diameter,[13] and the result taken as the drop diameter.

The actual rate of tracer in the treatment solution was determined by placing either 60 (≈ 200 μm diameter) drops (≈ 500 μm ml^{-1}) or 100 drops (≈ 2000 μg ml^{-1}) in 10 ml distilled water. These solutions were analyzed fluorimetrically, and the resulting fluorescence value was used to determine the concentra-

tion in $\mu g\ ml^{-1}$ in the 10-ml sample by using previously derived calibration curves.[15] Using this concentration, the drop number (60 or 100), the size applied, and the dilution factor, the treatment solution concentration was determined.

The total amount of tracer (μg) applied to each sample was determined by first determining the total volume of treatment solution contained in the drops applied. This is calculated from the drop diameter as determined from the water-sensitive paper analysis. The total volume applied (ml) multiplied by the treatment solution concentration ($\mu g\ ml^{-1}$) yields the total μg applied [Volume (ml) × Concentration ($\mu g\ ml^{-1}$) = Total μg].

To determine the recovery curves, the total applied (μg) to each dosimeter was plotted against the resulting fluorescence value of the extraction solution for that sample adjusted for background). Note that this fluorescence reading was only for the amount of tracer in solution, and did not reflect the tracer remaining on the sample. This may be verified by interpolation using the fluorescence value in the appropriate calibration curve. The resulting value, in $\mu g\ ml^{-1}$, readily converted to μg per sample, will normally be less than the μg applied, reflecting the extraction efficiency. This problem was avoided by plotting the fluorescence values against the μg applied, as described above. Thus, the resulting fluorescence value now accounted for 100% of the tracer actually present on the target before extraction, within limits of the measurement accuracy. The mean percentage recovery by the material was calculated by dividing the slope of the recovery curve by the slope of the calibration curve for each given scale/filter combination used on the fluorimeter.

4.2 Capture efficiency of a standard dosimeter

Washed muslin was chosen as the standard dosimeter material. As a first step, recovery curves for the dosimeter material were prepared as for the backup screens. For each test run, a sample of washed muslin 2·2 × 2·2 cm was attached to the dosimeter holder at the opening of the CETD, and the CETD placed in the wind tunnel. The atomizer used was an 'Ulva'® spinning disc sprayer (Micron Sprayers, Bromyard, UK) producing the spray size spectrum shown in Fig. 2. The tunnel was turned on, and allowed to come to speed, 5·5 m s^{-1}, before the spray was turned on, as described above. The atomizer was run for 8 s, the sprayer and tunnel were turned off, and the CETD removed. The test dosimeter and the backup screens were then removed from their holders and placed in snap-cap jars for fluorimetric analysis. Ten replicates were performed. Fluorimetric and statistical analyses were then conducted as described above, and the estimate of the capture efficiency, E, of washed muslin calculated.

4.3 Effect of sample size on efficiency

The most obvious effects of a violation of the assumptions will be manifested in a dependence of the efficiency on the size of the sample. For a given concentration flux of chemical in the air, the sample size, the amount the screens extract is dependent on only two factors: the duration of exposure and the airspeed (amount passing through the each screen per unit time). An important point is that sample efficiency should be independent of the amount of material intercepted by the sampler regardless of the exposure time. Some measures of efficiency are based on the amount taken by the sampler, and thus are dependent on both the air speed and the duration to use. To test the dependence of E on sample size, muslin patches were exposed in the wind tunnel for 4, 6, 8, 10 and 12 s. Five replicates at each time were conducted. The treatments (time) and replicates were completely randomized. The efficiency was computed and plotted against total amount captured. The experimental procedures, fluorimetric, and statistical analyses were performed as before.

5 RESULTS AND DISCUSSION

Figure 3 (open squares) shows how the quantity of tracer captured by the sampler's backup screens, m_s, declined exponentially with sample number, s. The values plotted in Fig. 3 are the mean mass (μg) of tracer recovered at each sample station in 10 runs. The estimated mass of tracer recovered in each run was derived from three colorimetric readings. The standard errors are smaller than the boxes on the figure.

Applying eqn (8), x_s was calculated from m_s, for each sample. Plotting n_s against x_s (Fig. 3, solid squares) results in a straight line with gradient $-\hat{q}$. The intercept on the abscissa gives the estimate of the population of droplets incident on the first screen, $\hat{M}$. Least squares linear regression of M_s on x_s resulted in estimates of the x-intercept, $\hat{M} = 1{\cdot}29$ and gradient, $\hat{q} = 0{\cdot}69$. Using these values to start iterative solution of eqns (10) and (11) resultant in exact ML estimates of $\hat{M} = 1{\cdot}74$ and $\hat{q} = 0{\cdot}67$. Using eqn (14), approximate ML estimates $\hat{M} = 1{\cdot}70$ and $\hat{q} = 0{\cdot}70$ were obtained which did not differ from the exact values by more than 4% (Table 2). The variances were all comparable to the estimates. All three methods gave estimates of capture efficiency which differed by only 1%; $-0 > 331 \leq E \leq -0{\cdot}327$ ($46{\cdot}6\% \leqq E' \leqq 47{\cdot}1\%$).

The results of the second experiment were a set of capture efficiencies of washed muslin dosimeters intercepting 'Tinopal'-marked spray for exposure times ranging from 4 to 12 s. Plotting the quantity of tracer recovered from the dosimeters against exposure time showed that amount of spray intercepted by the sampler, n_s, increased linearly with time over the duration of the experiment (Fig. 4, solid squares; $b = 0{\cdot}14$,

TABLE 2
Results of Removal Sampling Analysis with Washed Muslin

	Parameter estimates[a]					
Fitting method	p	$V[p]$	M	$V[M]$	E	E' (%)
Least squares	0·309	0·307	1·294	1·579	−0·327	47·1
Approximate ML	0·300	0·334	1·315	1·700	−0·330	46·8
Exact ML	0·297	0·334	1·322	1·744	−0·331	46·6

[a] p is the probability of capture of an individual droplet by the CETD, M is the amount of spray incident on the dosimeter, $V(\cdot)$ are their variances, E and E' are measures of capture efficiency and are related by eqn (2). (See Sections 3.2.1 and 3.2.2).

$F_{1,25} = 151$, $\alpha < 0{\cdot}001$). However, the capture efficiency, E, was found to be independent of time exposed (Fig. 4, solid squares; $r^2 = 0{\cdot}0001$). Consequently, E was also effectively independent of exposure time (Fig. 4, inset; $r^2 = 0{\cdot}04$).

The time the test dosimeters spent in the wind tunnel exposed to simulated pesticide spray was, of course, substantially less than that during which a spray applicator would be exposed to drifting pesticide while spraying a cornfield. However, 16–19 km h^{-1} (9–10 knots) is probably the upper limit of wind speed at which an operator would apply any pesticide. Thus the wind speed in the wind tunnel (5·5 m s^{-1} or 20 km h^{-1}) represents the upper limit of practical conditions for spraying. In fact, one would prefer to spray in much stiller air, say <2 m s^{-1}.

No variation in efficiency was evident over the short period, 4–12 s, of exposure, and provided that the dosimeter never becomes saturated, the efficiency should remain constant.

These experiments were conducted using the fluorescent tracer, 'Tinopal', in water, rather than an actual pesticide formulation. The reason for this is simple: to avoid contamination of the wind tunnel with chemicals which could ultimately make it unusable. In addition, the air passing through the tunnel is eventually vented to the outside, and unnecessary chemical pollution is not warranted. We must therefore work with a simpler aerosol model than would be ideal. Clearly the physicochemical composition of the spray cloud must influence the attachment rate of droplets to a dosimeter surface. The addition of spreader-stickers and other adjuvants is intended to increase the likelihood of a droplet attaching itself to any surface with which it comes in contact. We have no evidence that droplets were bouncing off the test dosimeter or backup screens, nor that droplets were breaking up or coalescing in the CETD. If bouncing, breakup or coalescence were happening, or the air-speed in the CETD was dropping substantially, we would expect a significant 'fallout' of droplets between the screens. We were unable to detect any tracer with water-sensitive paper inside the CETD, which strongly suggests that fallout was rare.

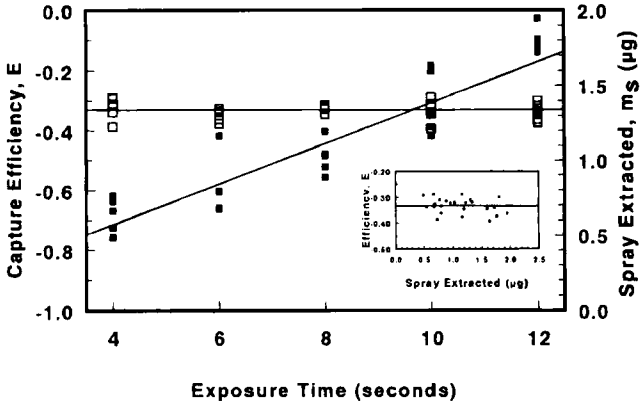

Fig. 4. The sampling efficiency of the muslin patch dosimeter is independent of the time exposed (open squares), even though the total amount of spray captured increases linearly with exposure time (solid squares). The capture efficiency is therefore independent of the amount of spray captured (inset).

The issue here is whether the droplets contact the dosimeter in the first place, and this is dependent on the velocity and mass (kinetic energy) of the droplets. In our test situation, we made the spray cloud as uniform in size and velocity as possible. A real-world spray cloud from a hydraulic nozzle is composed of a much wider range of drop sizes and speeds. Thus, it is the simplification of near-uniform kinetic energy which may not translate well to the field, not the spray composition (pesticide plus adjuvant).

Although the majority of pesticides are applied using directed sprays, a significant proportion of the spray applied arrives on the target foliage and in some cases the target pest by virtue of the ability of the foliage or pest to capture passively droplets from the passing spray cloud. The amount of spray (especially that contained in small droplets) that eventually impinges upon the target is determined partly by the capture efficiency of the target. It is well documented that small cylindrical targets such as stems or twigs have a higher capture efficiency than flat targets. Similarly, hairy targets are more efficient collectors of droplets than smooth ones. We are currently applying these methods to a comparison of dosimeter materials and geometries.

The techniques discussed herein lend themselves admirably to the experimental goals of accurately studying the capture and collection efficiency of all types of possible target substrates, both natural, as plant material, or artificial. Thus we envisage the device being utilized in pesticide exposure studies as well as pesticide drift studies of windbreak efficiency. Furthermore, the use of live insect targets can be considered. The technique could be adapted for use with tethered locusts, for example, which may be suspended in an airstream containing pesticide droplets or tracer in order to investigate novel application or insecticide systems. Thus, it may be possible to use the technique for investigating the capture efficiency of all manner of pests in a controlled environment and with less wastage of sprayed material than has been hitherto possible.

The CETD could be used directly to estimate exposure in the field. The CETD and its backup screens should behave in the field exactly as in the wind tunnel. Thus, provided the CETD moved with the human operator (on the tractor), the amount of pesticide to which he had been exposed could be determined from the ratio of the spray recovered from his dosimeter to the efficiency of a dosimeter in the CETD. Because we now have the potential for measuring absolute capture efficiency, dosimeter standards can be defined, making it possible to create a standard dosimeter which, like radiation badges, would become part of the spray application apparatus.

The technique described here represents a novel approach toward determining capture efficiency. Previous methods relied on an accurate and precise knowledge of the amount of material that passed through a given area within the test device, determined by a knowledge of the atomizer output, to calculate the efficiency. The proposed method does not have this requirement, making the system much more flexible in terms of run times used, drop sizes that may be used, amounts of spray material introduced to the test device, and location, as well as the important potential for using the device in greenhouse, field, or forest.

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